



INTEX/ICARTT Hydrogen Peroxide Methylhydroperoxide

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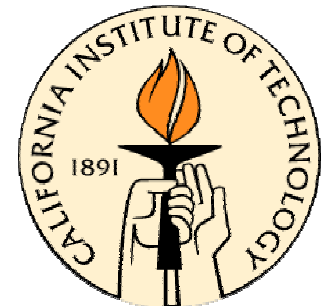
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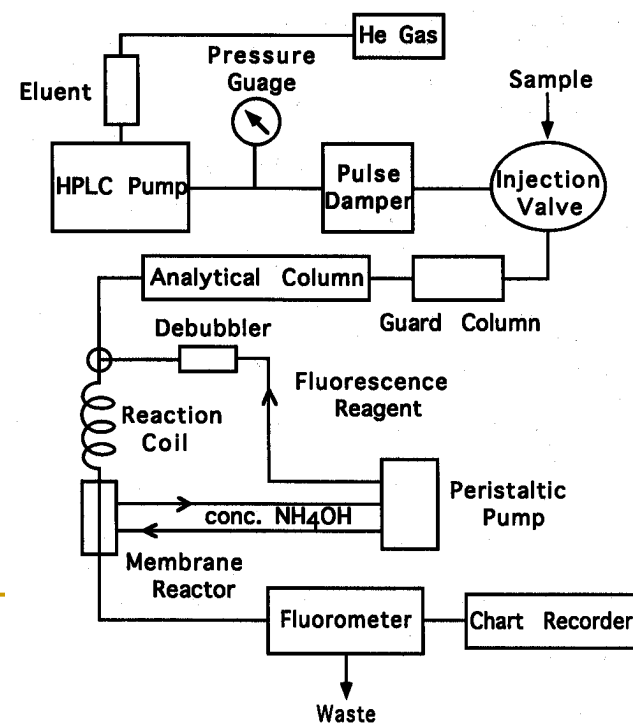
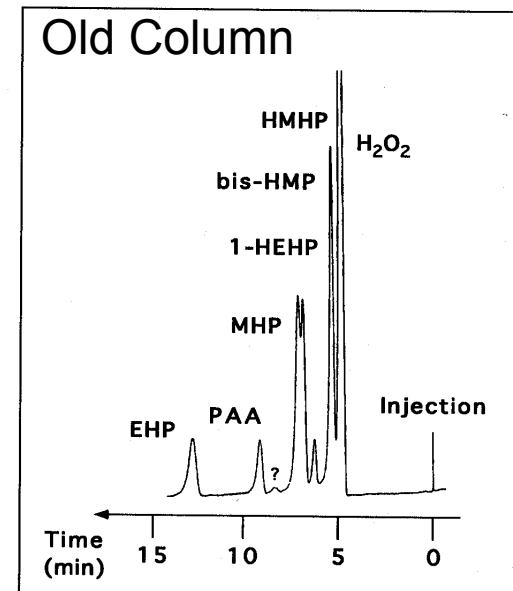
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Peroxide Analytical System

- → Peroxides separated on a C-18 column
- → Undergo post column derivatization w/ 4-hydroxyphenyl acetic acid
- → Form a fluorescent dimmer.
- H_2O_2 and CH_3OOH are separated in about 1 minute
- Sampling frequency = 75 sec.
- DL for H_2O_2 is <10 pptv.
- DL for CH_3OOH is <25 pptv.

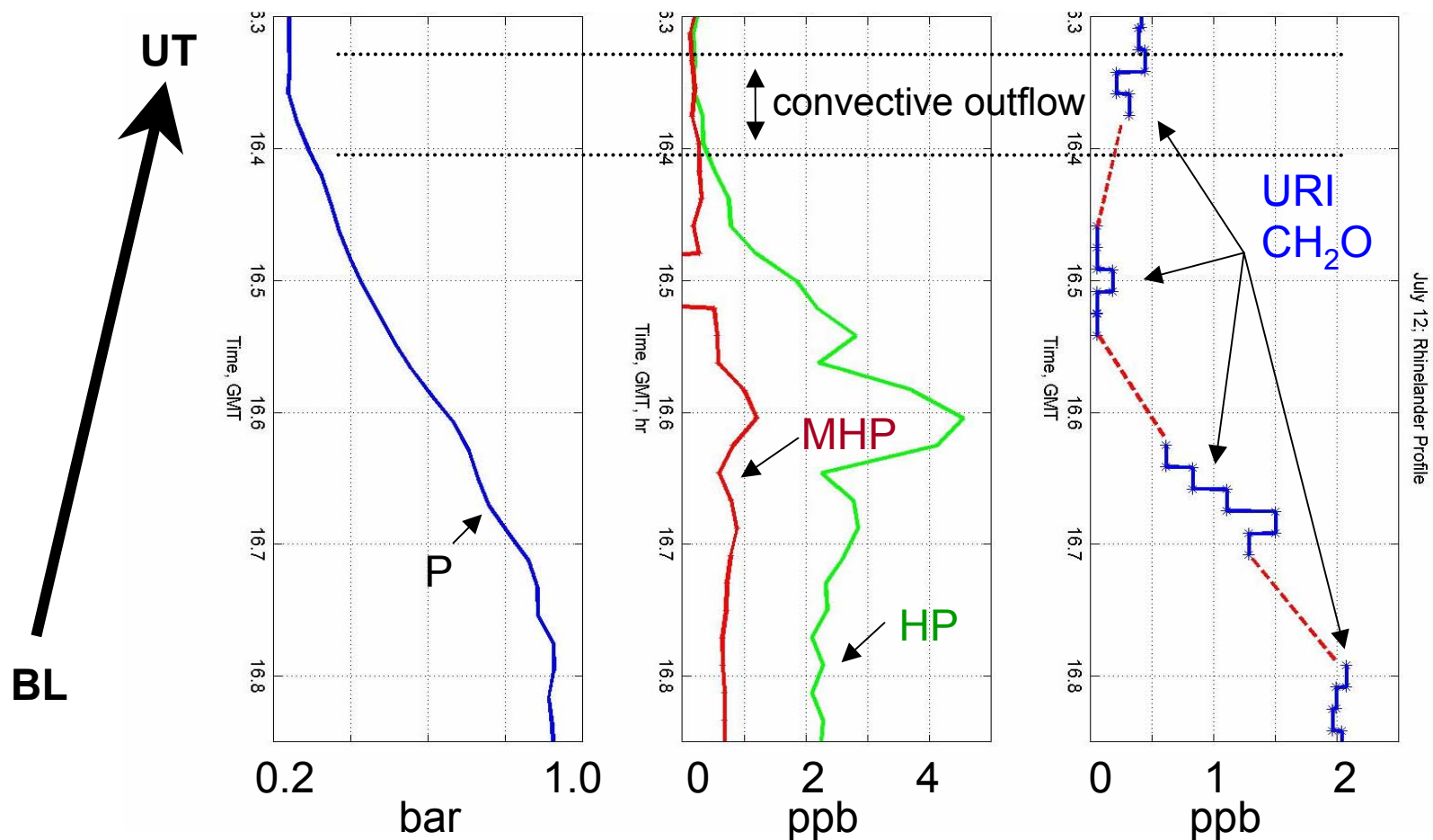


Preliminary Results: Hydrogen Peroxide (HP) and Methylhydroperoxide (MHP)

- Cleaner and clearer marine Concentrations (Eastern North Pacific):
 - HP and MHP at 1 and 2 ppbv in MBL
 - HP/MHP Ratio ~ 1
- Continental BL
 - HP ~ 1.5 to 3 ppbv, MHP ~ 1-1.5 ppb for MHP;
 - HP/MHP Ratio ~ 2 to 4
- Lower-troposphere above BL
 - Higher HP → in excess of 4 ppb
 - Maxima above 7 ppb (Flt 7) and 8 ppb (Flt 9).
- Fire Plumes (Flt 9)
 - HP >3 and MHP >2 ppb.
- In many samples a “3rd” peroxide peak is present.

Tests underway to evaluate it as peracetic acid: aka PAA

DC-8 Preliminary Data; Rhinelanders WI Spiral – Point “B” on Map, July 12, 2004



Upper troposphere (UT) shows evidence of convective outflow (convect); elevated CH_2O and elevated CH_3OOH relative to H_2O_2 .

Figure 3



Preliminary Data; DC-8 Flight 3, Eastern North Pacific; July 1, 2004

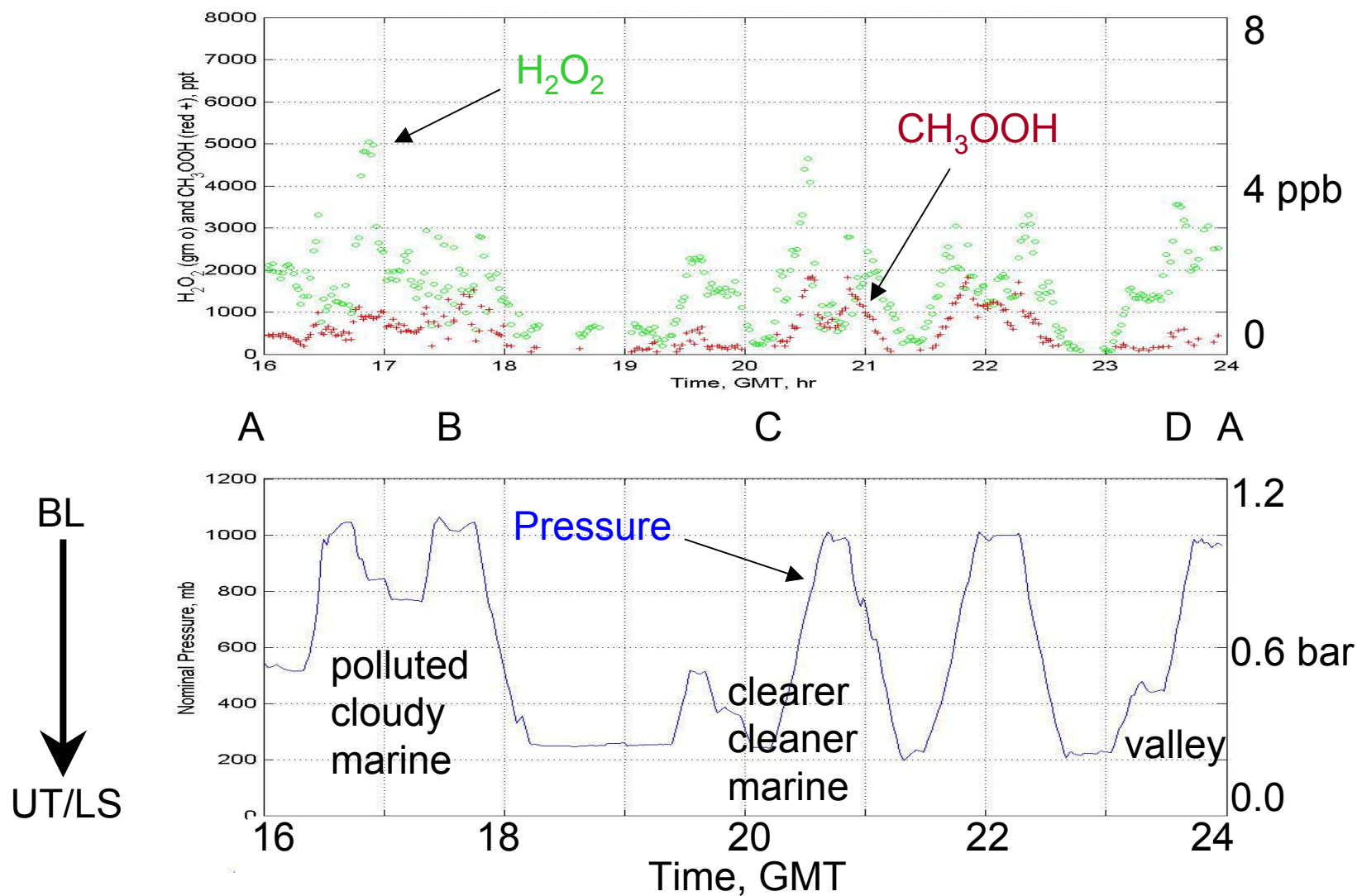
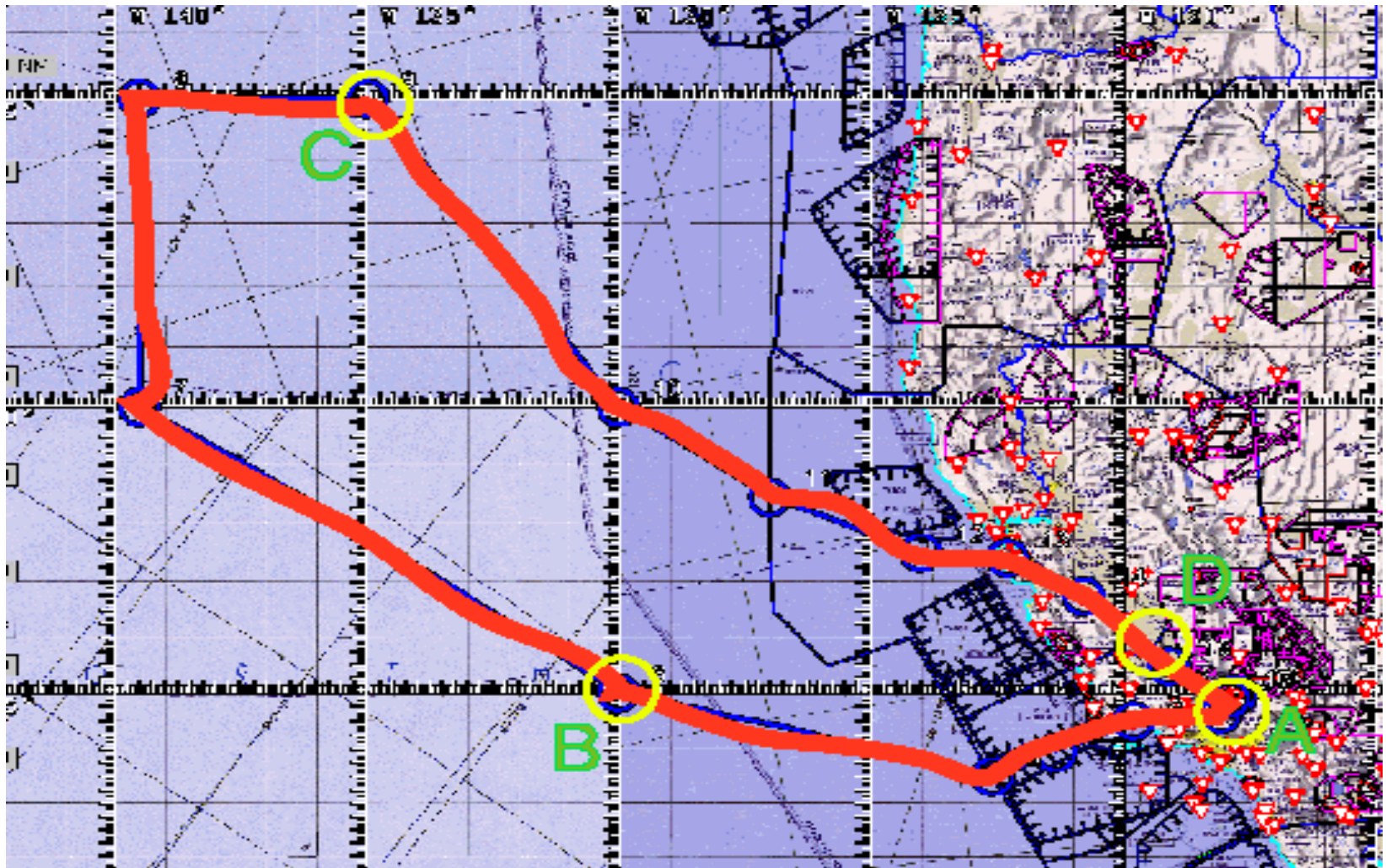


Figure 1a



DC-8 Flight 3; Eastern North Pacific; July 1, 2004
Letters refer to locations on fig. 1a

Figure 1b

Preliminary Data; DC-8 Flight 7, Circumnavigation Eastern US; July 12, 2004

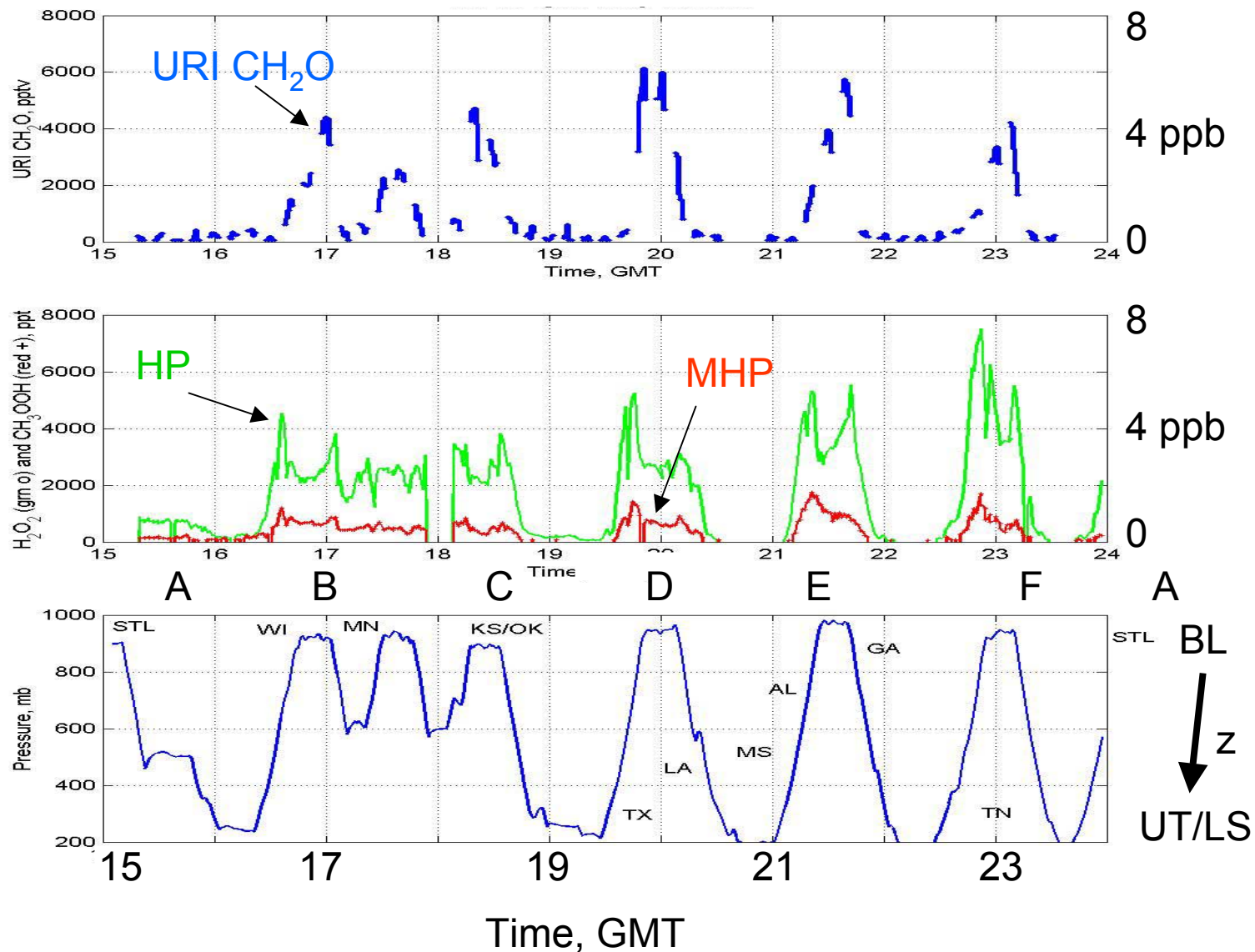
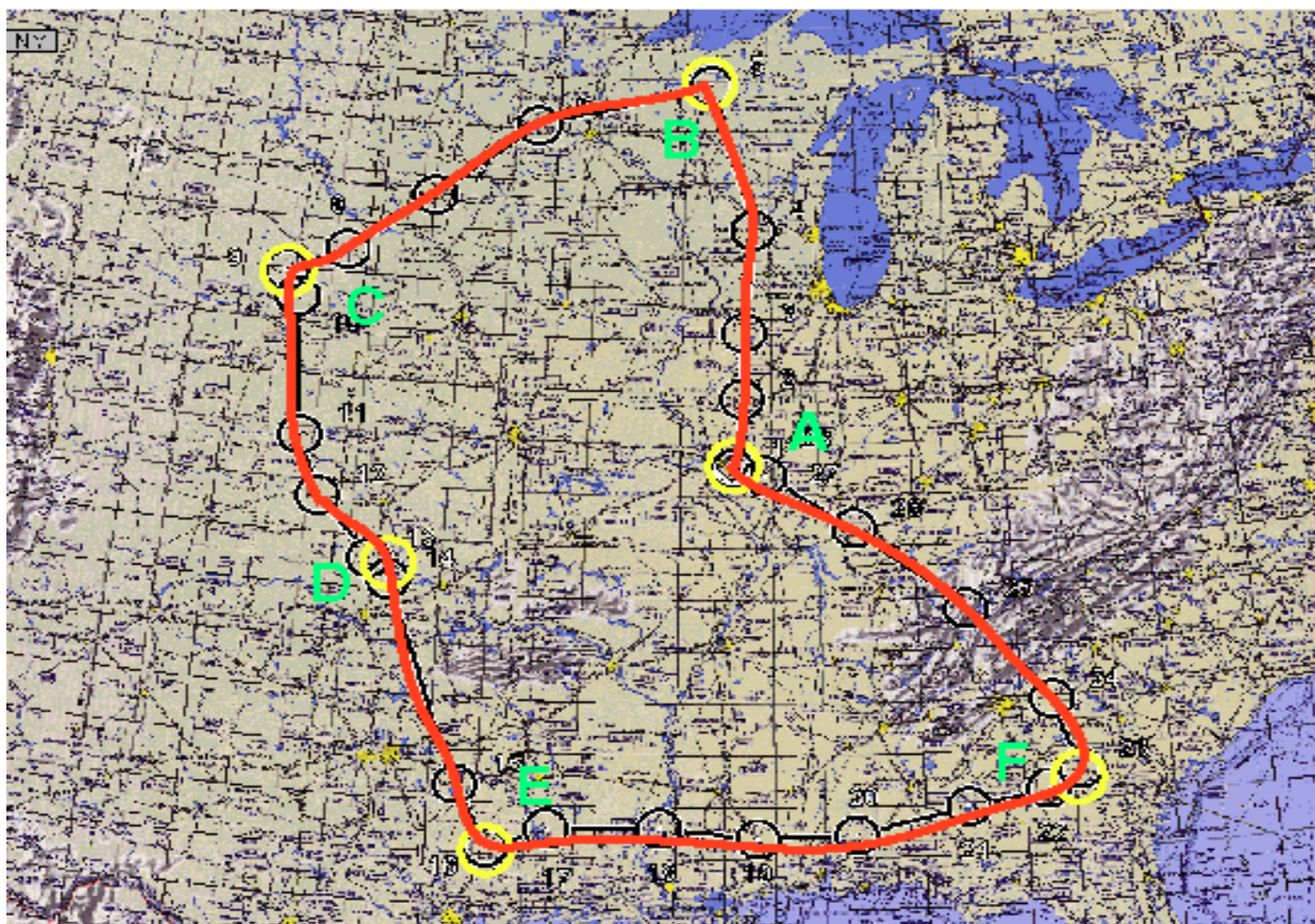


Figure 2a



DC-8 Ground Track (Flight 07); July 12, 2004
Letters correspond with those shown on fig. 2a.

Figure 2b

Preliminary Results Hydrogen Peroxide (HP) and Methylhydroperoxide (MHP), cont.

Initial **VERY FRIENDLY** comparison of peroxides measured by HPLC (URI-USNA Group) and CIMS (Wennberg & CalTech Group) shows:

1. Very good agreement (within stated accuracy and precision) in trends and values for HP. (see Figure 4)
2. HPLC “3rd” peak trends correspond with trends in a CIMS m/z ion consistent with that expected for PAA.
3. HPLC and CIMS groups continue to work on HP and MHP comparison and the confirmation and calibration of PAA and HMHP.

DC-8 Preliminary Data; H₂O₂ Comparison; Flight 7; July 12, 2004

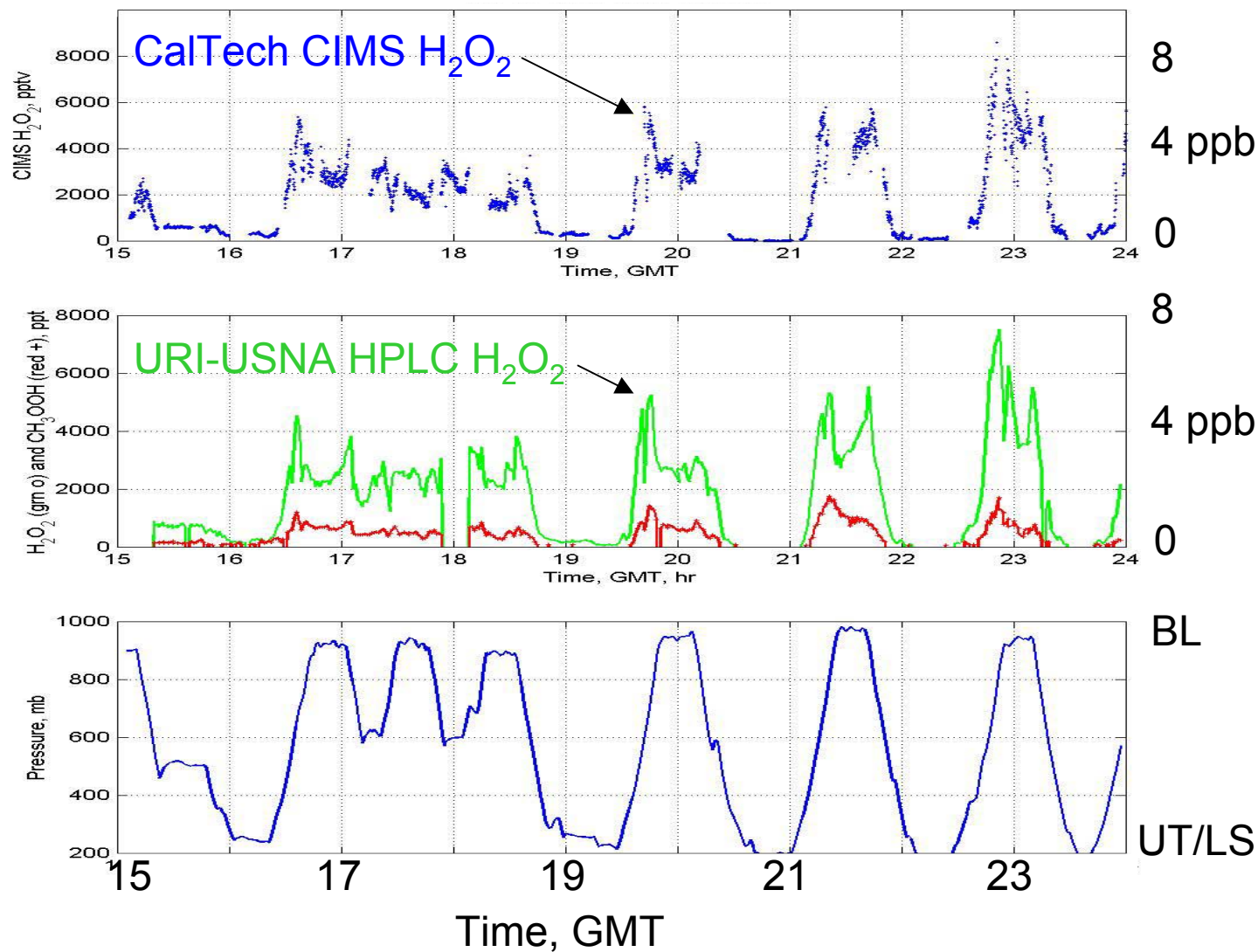


Figure 4

Preliminary Results Hydrogen Peroxide (HP) and Methylhydroperoxide (MHP), cont.

- New columns run “faster” allowing 30 s samples at 75 sec intervals
- Upside - better temporal resolution
- Downside - loss of peroxide species resolution, e.g., HP from hydroxymethylhydroperoxide, aka, HMHP
- Tests with “slow” column on flight 10 suggested HMHP was NOT present at significant levels over forested areas; areas where it has been suggested HMHP is present at levels comparable to HP
- Column tests will continue on a flight-by-flight basis